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6. AUTHOR(S)

Frank D. Blum

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

University of Missouri-Rolla
Department of Chemistry
Rolla, MO 65401
ATTN: Frank D. Blum

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Office of Naval Research - Code 5000
Chemistry Division
800 Quincy Street
Arlington, VA 22217
ATTN: Kenneth J. Wynne

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Dynamics of the Interface
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by

<u>Frank D. Blum</u>

Department of Chemistry and Materials Research Center
University of Missouri-Rolla
Rolla, MO 65401

(314) 341-4151

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DYNAMICS OF THE INTERFACE IN A MODEL COMPOSITE SYSTEM

Frank D. Blum

Department of Chemistry and Materials Research Center, University of Missouri-Rolla, Rolla, MO 65401, USA

Abstract: A review of recent experiments from the authors laboratory on the dynamics of aminofunctional silane coupling agents is given. Of special emphasis are two coupling agents, aminopropylsilane (APS) and aminobutylsilane (ABS) which were deuterated in the γ-position. These two coupling agents have similar chemical behavior, but different dynamics. Deuterium NMR studies reveal that the APS moves slower on the silica surface than ABS. The mobility of the interfacial ABS was also found to be significantly slowed when it was overcoated with a polymerized layer of bismaleimide to form a composite. When the composite was treated with water, the interfacial mobility of the ABS increased. The flexural strength of the APS treated composite was the highest compared to ABS-treated and bulk glass in an epoxy-glass composite.

INTRODUCTION

One of the most important uses of synthetic polymers is in filled systems, including composites. The properties of these composites depend not only on the properties of the components, but also on the properties of any interfacial material present. This material is typically found in very thin layers, often on the order of Ångstroms, so that its characterization is difficult by typical mechanical techniques. Spectroscopic techniques, however, can be used to study these layers. Of the spectroscopic techniques available, NMR has the advantage of being: relatively non-perturbing; relatively insensitive to the optical clarity or filled nature of the material; and able to be selectively labeled for contrast. Weighed against this is the inherent insensitivity of the NMR experiment.
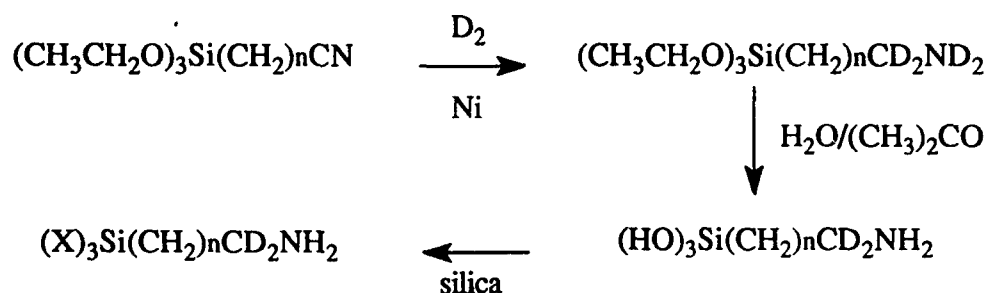
In the present paper, we review work from our laboratory on the dynamics of two coupling agents on a silica surface and in a composite material. The coupling agents are specifically labelled with deuterium so that their dynamics can be probed in the presence of an overlayer of polymer. These two coupling agents have chemistries which should be very similar. They are believed to differ mainly in their mobilities. There are four major effects to be probed: i) the differences in mobility of two coupling agents on silica; ii) the effects of

overpolymerization on the interfacial layer; iii) the effects of moisture on the coupling agent layer; and iv) the correlation of the dynamical properties on the physical properties to composites.

The scope of this paper is limited to work done in our laboratory. Much of the work by others has been reviewed and the reader is referred to these for a summary of other NMR work including: polymers at interfaces (Ref. 1); the use of isotopes for the studies of polymers and surface active agents at interfaces (Ref. 2); and organic thin films at interfaces (Ref. 3). These give an overview of the studies that have been performed on interfacial species in terms of both the structure and dynamics. In addition, the earlier spectroscopic work on coupling agents has been reviewed by Ishida (Ref. 4).

EXPERIMENTAL

The synthetic route for the production of the coupling agents used was:

$$(CH_3CH_2O)_3Si(CH_2)nCN \xrightarrow[Ni]{D_2} (CH_3CH_2O)_3Si(CH_2)nCD_2ND_2$$

$$\Big\downarrow H_2O/(CH_3)_2CO$$

$$(X)_3Si(CH_2)nCD_2NH_2 \xleftarrow[silica]{} (HO)_3Si(CH_2)nCD_2NH_2$$

The coupling agents used were aminopropylsilane (APS) and aminobutylsilane (ABS). These specifically-deuterated materials (DAPS, n = 2 and DABS, n = 3) were prepared from the appropriate cyano-precursors treated with deuterium gas (Ref. 5). Typically, the triethoxysilane ester was used, but occasionally the trimethoxy group was also used. Deuteration of the cyano-group gives both methylene and amino-labelled deuterons. Subsequent treatment with H_2O or H_2O/acetone both hydrolyzes the silane as well as exchanges the amine deuterons for protons (Ref. 5). The silane hydroxyl then reacts with other coupling agents or surface groups to form Si-O-Si linkages. In the idealized reaction scheme above, X may represent a variety of different species including -OCH$_2$CH$_3$, -OH, or -OSi-.

The silica surface used was a high surface-area fumed silica, Cab-O-Sil (normally S-17 with a surface area of 400 m^2/g). Prior to use, it was dried under vacuum at 120 °C for 2 days to remove moisture. This treatment did not affect the surface area or adsorption behavior of the coupling agent.

For the deposition of the coupling agents onto the silica surface, silane treating solutions of different concentrations were prepared. Silica was placed in a test tube and treated with an

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aliquot of freshly prepared coupling agent solution in water. The solution was left in contact with the silica for a few hours with occasional agitation using a vortex mixer. After that, the sample was centrifuged at about 3000 rpm for 1 h, washed twice with distilled water and then dried in a vacuum oven at about 90 °C overnight.
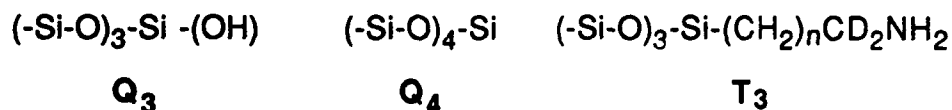
The NMR experiments were performed on a Varian VXR-200 NMR spectrometer. The solid-state ^{29}Si NMR spectra were obtained at frequency of 39.7 MHz with cross-polarization and magic-angle spinning (CP/MAS) using a Varian PLE probe with zirconia stator and vespel rotor. Magic-angle spinning at 2.7 kHz, cross-polarization with a contact time of 2.5 ms, recycle delay time of 3 s, 90° pulse width of 10 ms, and high-power proton decoupling of 44.6 kHz to remove proton dipolar broadening, were used. The spectrometer was also equipped with a wide-line probe operated at a deuterium frequency of 30.7 MHz. All ^{2}H NMR spectra were collected using a variant of the solid-echo pulse sequence with the 180° prepulse and subtraction used on each alternate scan.

$$[180° - (\text{alternate pulse}) - \text{delay} - 90°_x - \tau_1 - 90°_y - \tau_2 - \text{echo}]$$

This entire sequence was also phase cycled and has the effect of reducing coherent noise and acoustic ringing while coherently adding the nuclear signals. For all of the ^{2}H NMR spectra, a delay time of around 20 µs, τ_1 of typically 30 µs, repetition time of about 2 s, and 90° pulse width of 2.0 µs were used. The value of τ_2 was usually set to about 10 µs less than τ_1 and the spectra were left shifted to start the transforms at the points of maximum intensities of the echos. Typically 2,000-10,000 echos were required per spectrum, depending on the sample. No attempt was made to correct the spectra for finite pulse widths.

RESULTS AND DISCUSSION

The chemical bonding of the coupling agent to the silica is deemed to be an important factor in its effectiveness (Ref. 6). ^{29}Si CP-MAS NMR was shown diagnostic of the bond formation (Ref. 7). For the reaction of DABS on silica, ^{29}Si spectra (Ref. 4) of the silicons at the surface showed that the silanol (Q_3, -102 ppm) resonance intensity decreased while that of the Q_4 (-110 ppm) resonances increased. In addition the appearance of resonances from the X_3Si-R (T_3, -67 ppm) groups indicated the presence of the coupling agents at the surface.

$$(\text{-Si-O})_3\text{-Si -(OH)} \qquad (\text{-Si-O})_4\text{-Si} \qquad (\text{-Si-O})_3\text{-Si-(CH}_2)_n\text{CD}_2\text{NH}_2$$

$$\mathbf{Q_3} \qquad\qquad \mathbf{Q_4} \qquad\qquad \mathbf{T_3}$$

The dynamics of both DAPS and DABS on silica have been probed at the solid air-interface with deuterium NMR. DAPS and DABS are similar chemically and differ mainly in the number of carbons in the chain. Any chemical change also alters the chemical properties, but in this case, we believe that the major effect of the different coupling agents is in the dynamics. The spectra of these two coupling agents attached to the surface from solutions of

different concentrations were taken (Ref. 8). Under the adsorption from acetone-water mixtures, a "monolayer" coverage was deemed to be adsorbed from a 2 wt % solution of the coupling agent (Ref. 9). Of course the exact nature of this monolayer is complicated because of the presence of oligomers in solution and the multifunctional nature of the coupling agent. Nevertheless, several things can be learned from a comparison of the dynamics at different coverages.

Shown in Fig. 1 is a comparison of the ^2H quadrupole echo spectra of DAPS and DABS (Ref. 9) at different treating solution concentrations. A detailed analysis of the spectra has been given (Ref. 9) and only the main points will be emphasized here. The spectra from 2 wt % treating solution show the broadest spectrum consistent with the most rigid system. The spectra are complex, but can be adequately modelled by assuming i) a rigid component, ii) a component which undergoes two-site conformational jumps, and iii) a component which undergoes an anisotropic rotational diffusion. At concentrations below 2 wt%, the spectra are narrower because the coupling agents have more mobility because there is incomplete surface coverage and more room for the molecules to move. At higher coverages, multilayer formation occurs and the multilayers have more mobile behavior than the initially-bound layer. With the exception of the coupling agents from the highest concentration (10 wt%), there is remarkable similarity between the DAPS and DABS. From the higher concentrations in solution, the deposited material show spectra which are similar to those of the bulk-polymerized polymer (Ref. 10). This was indicative of a higher mobility of the bulk vs. surface-bound coupling agent. DABS in these multilayers appears to move about a factor of 10 faster in the 10 wt% treated sample.

The second question answered with deuterium NMR techniques was how the dynamics of the interfacial layer were perturbed by the presence of the polymer overlayer. To answer this question, a sample of DABS on silica was prepared with roughly the amount needed to form a monolayer on the surface. This material was then reacted with bismaleimide (BMI) and the polymer cured (Ref. 11). As shown in the reaction scheme below, bismaleimide reacted with the amine group of the coupling agent. This was verified by the reactions of model compounds and also solid-state ^{13}C NMR.
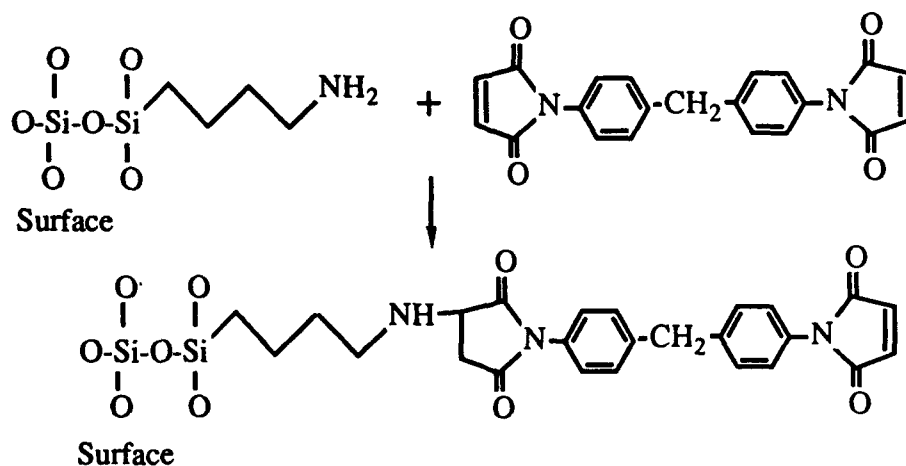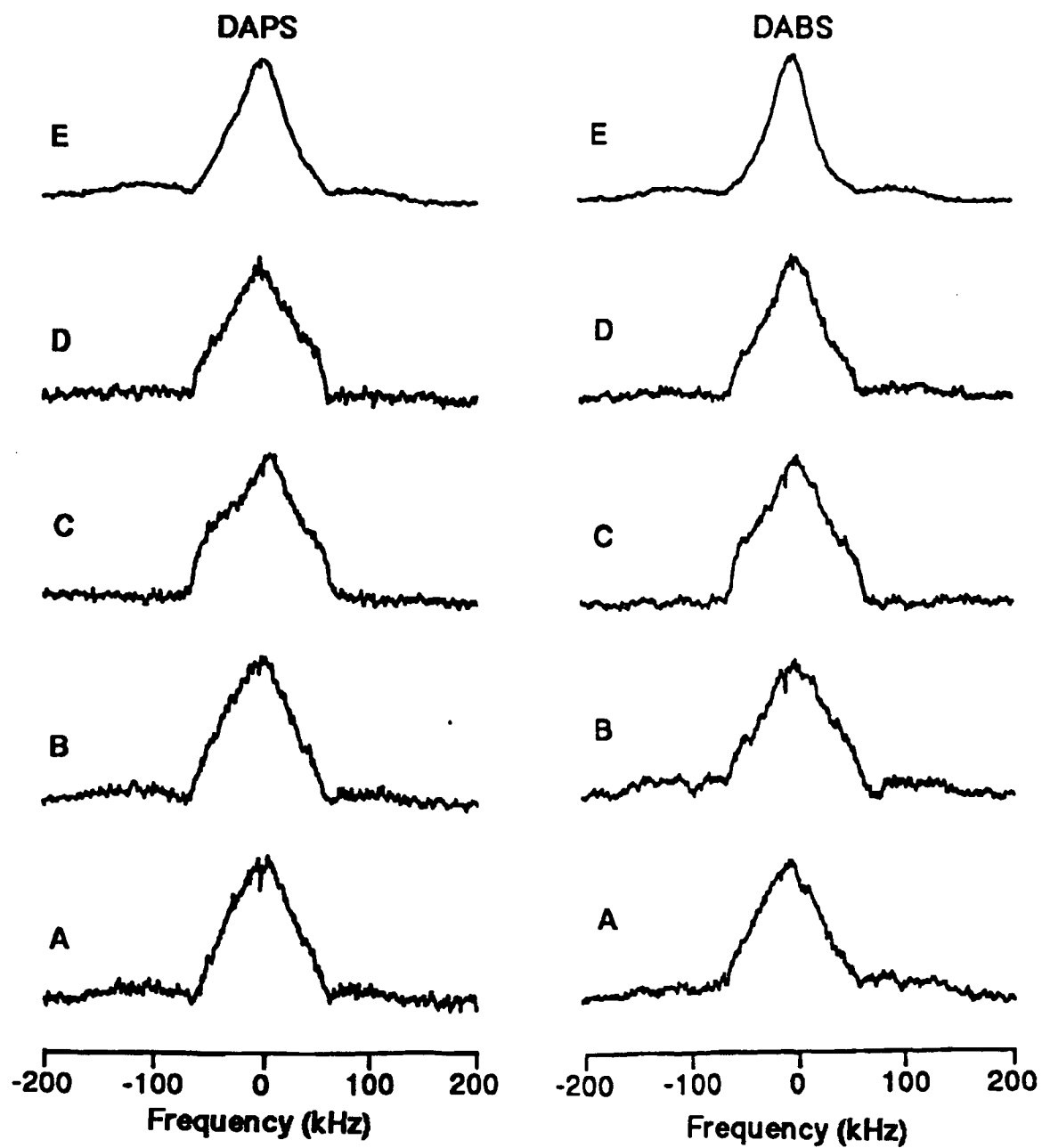
Fig. 1. Deuterium NMR spectra deuterium-labelled DAPS and DABS on silica. The material was deposited with solution concentrations of A) 0.5%, B) 1.0%, C) 2.0%, D) 3.5% and E) 10%; 2% corresponds to approximately monolayer coverage. (After Ref. 8).

A comparison of spectra from the DABS on silica with and without a BMI overpolymerized layer is shown in Fig. 2. As can be observed in the figure, the spectrum with the overlayer is broader. A comparison with spectral simulations reveals two interesting things. First, the mechanism of motion in the coupling agent layer is qualitatively different. The spectra can no longer be simulated if the overall anisotropic rotation is considered. However, the spectra can still be simulated with conformational jumps alone. This is consistent with the notion that reaction with the BMI supresses the wider-range motions of the chains and the chains are left to undergo only conformational jumps. Second, the frequency of these jumps is a factor of 5 faster in the initial system as compared to that of the overpolymerized one.
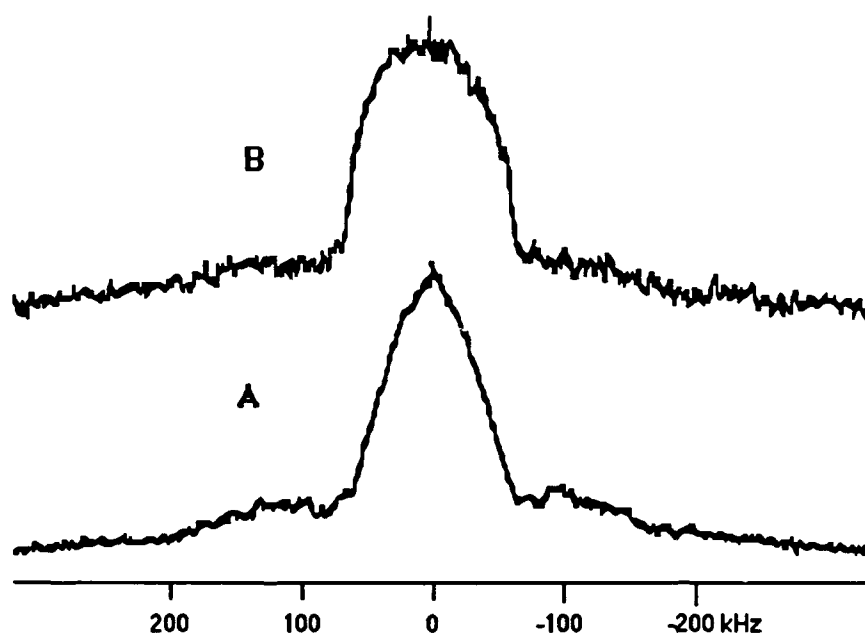

Fig. 2. Deuterium NMR spectra DABS at (A) monolayer coverage alone and (B) monolayer coverage, overpolymerized with bismaleimide. (after Ref. 11)

Since the interface could be selectively labelled, the effects of moisture on the interface could be monitored. To this end, samples of silica treated with DABS were overlayered with BMI. The initial sample is shown in Fig. 3A. After treatment with water, Fig. 3B results and it is significantly narrower than that of the dry sample. The very narrow component is probably due to the residual deuterons in the added water. From the spectra of the wet material it is apparent that the water penetrates and goes to the interface, speeding up the motion of the coupling agent. Simulations reveal that the coupling agent is speeded up by a factor of 4 over the dry sample (Ref. 12). In addition, the sample appears to return to its original state when it is dried (not shown, Ref. 12). A similar speedup (factor of about 4) was found for the coupling agent on the surface without the polymer overlayer.
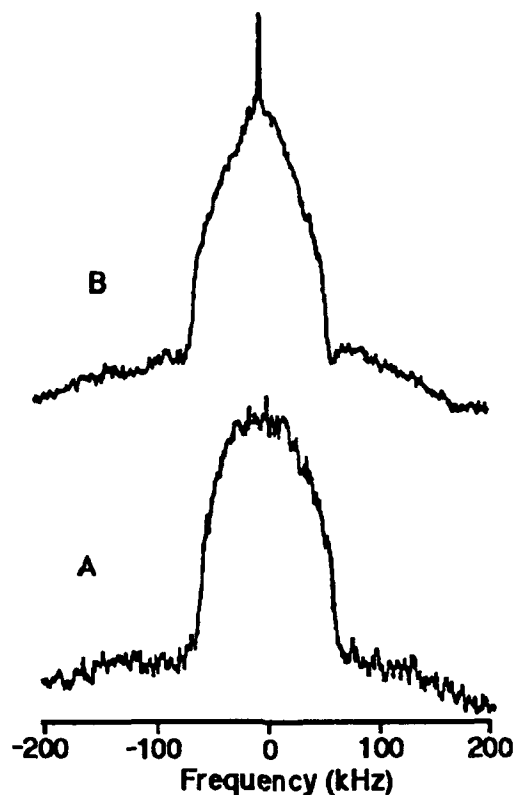
Fig. 3. Deuterium NMR spectra DABS at overcoated with BMI at monolayer coverage (A) as prepared and (B) wetted with H₂O. (after Ref. 12)

Finally, the question that is ultimately the most important is how do these experiments relate to the physical properties of composite materials. To answer this, a series of samples was prepared from layers of glass fabric and epoxy. The glass fabric was treated with the coupling agent solutions with a 2 wt % concentration. After passing the material through the solution, the fabrics were allowed to air dry producing multilayers of coupling agent. We examined a number of properties (Ref. 13) but will only focus on the flexural strength here. Three point bend tests were done, according to ASTM-D790, to establish these. Shown in Fig. 4 are the flexural strengths of three composites with different surface treatments in the wet and dry state. For the dry material, the flexural strengths of the composites were of the order APS > ABS > bulk. Thus the presence of the coupling agent at the interface increase the strength over the untreated one (bulk). Additionally, similar behavior has been observed for the wet strengths of the composites. The APS treated composite has the highest wet strength.

From the data presented here, an interesting picture emerges. The APS performed better in mechanical studies than ABS. We believe that this is due to the differences in mobility of the coupling agent layer at the coupling agent-polymer interface. We also believe that one additional reason why silane coupling agents work so well is illustrated by the APS system For example, the graded interface that is automatically formed on treated glass may be just the

appropriate gradation for the physical properties of each of the dissimilar materials (e.g. glass-epoxy).
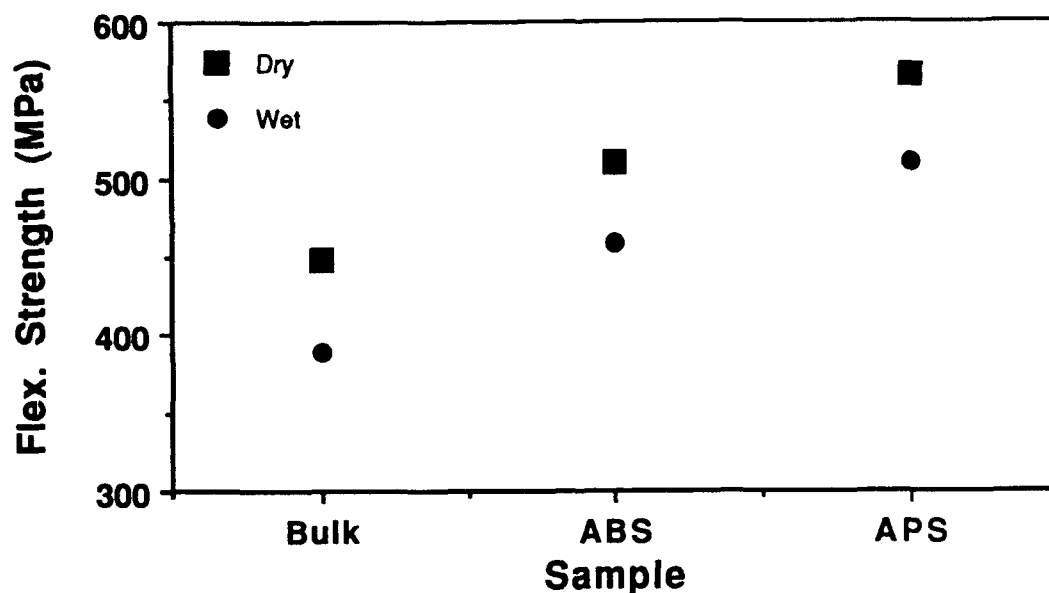

Fig. 4. Flexural strengths of epoxy-glass composites in the dry and wet strengths.

CONCLUSIONS

From our studies and (in part based on those of others) the following conclusions can be made:

1.   DAPS and DABS show similar behavior at monolayer coverage and just above and below this. We believe that this is due to similar structure and dynamics of the initial layer(s) at low amounts. At the apparent monolayer coverage, the spectra were the most rigid and the spectra at either side of this coverage were more mobile. The observed spectra could be modelled with rigid, jumping and anisotropically rotating component.

2.   At higher coverage (from 10 wt% treating solution) the dynamics started to resemble those of the bulk-polymerized coupling agents. The DABS spectra suggested that their motion was about 10 times faster than that of DAPS.

3.   The overpolymerization of surface-bound DABS with BMI polymer decreases the mobility and changes the mechanism of motion of the coupling agent. The overall motion of the coupling agent is eliminated and the molecule undergoes only conformational jumps. These are about a factor of five slower than the jumps observed in the material without the overlayer.

4.   When water is added to the composite with the labelled coupling agent, the water penetrated to the interface and was effective at increasing the mobility of the interfacial layer. The presence of water speeded up the interfacial DABS by about a factor of 4. The interface returned to its original state upon drying.

5. The flexural strengths of treated composites were greatest for the APS systems for both wet and dry samples. The higher strengths for the APS system over ABS system are believed to be due to the dynamics of the interfacial material. These studies point to the fact that in the selection and design of coupling agent systems, the dynamics of the interfacial layer needs to be considered.

ACKNOWLEDGMENTS

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